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GB 1445593
GB 1323710
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GB 1289889
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# (54) Method for maintaining activity of zeolite catalysts

(57) Zeolites used in catalytic conversion processes such as cracking, hydrocracking and dewaxing are activated by co-feeding (a) water and/or a water precursor and/or (b) hydrogen sulphide and/or a hydrogen sulphide precursor with the feedstock. Suitable water precursors include alcohols such as methanol, ethanol, propanol, butanol and pentanol. The method may be used to restore lost activity or maintain a given level of activity.

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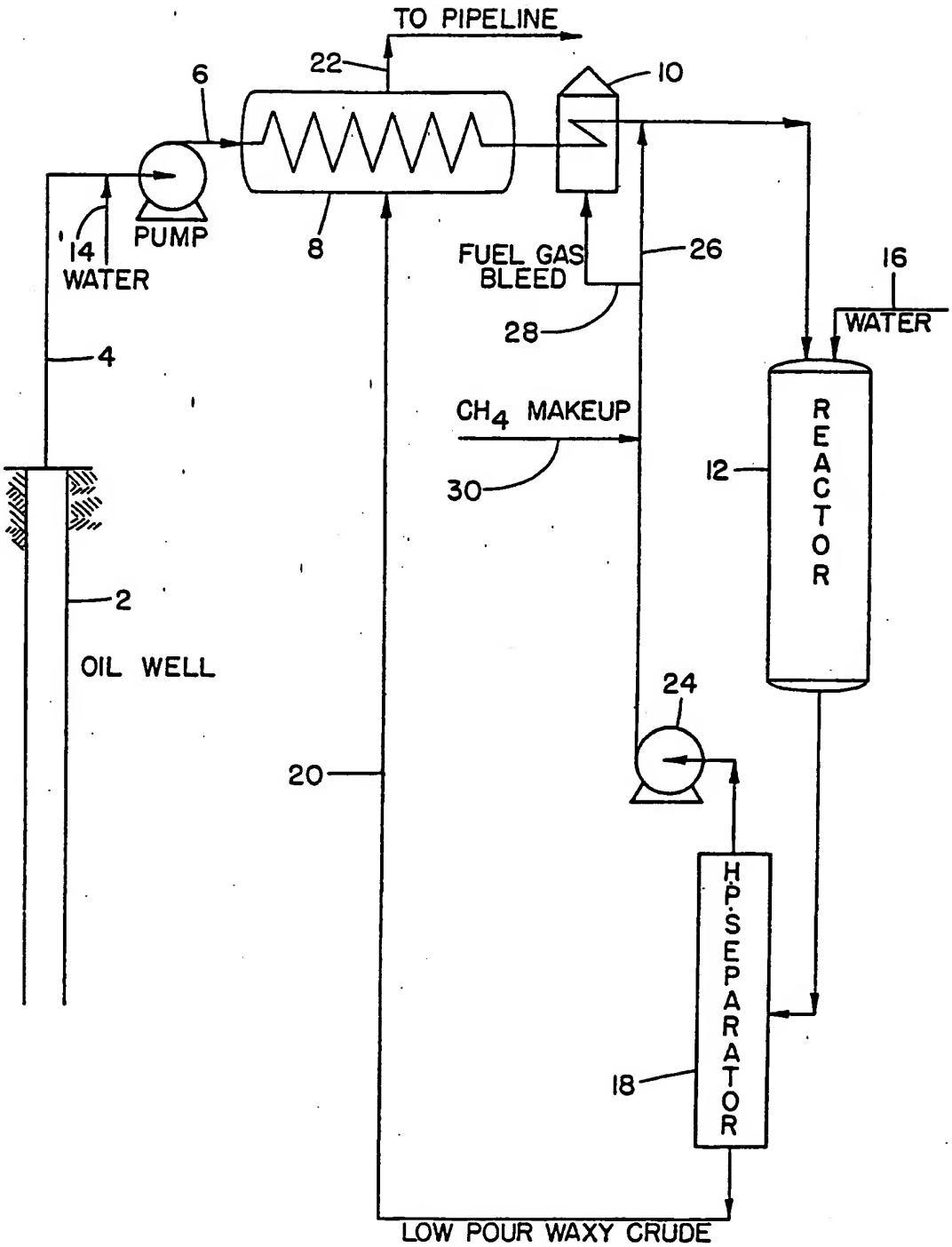
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22
6
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WATER
8
FUEL GAS
BLEED
26
16
WATER
28
4
$CH_4$ MAKEUP
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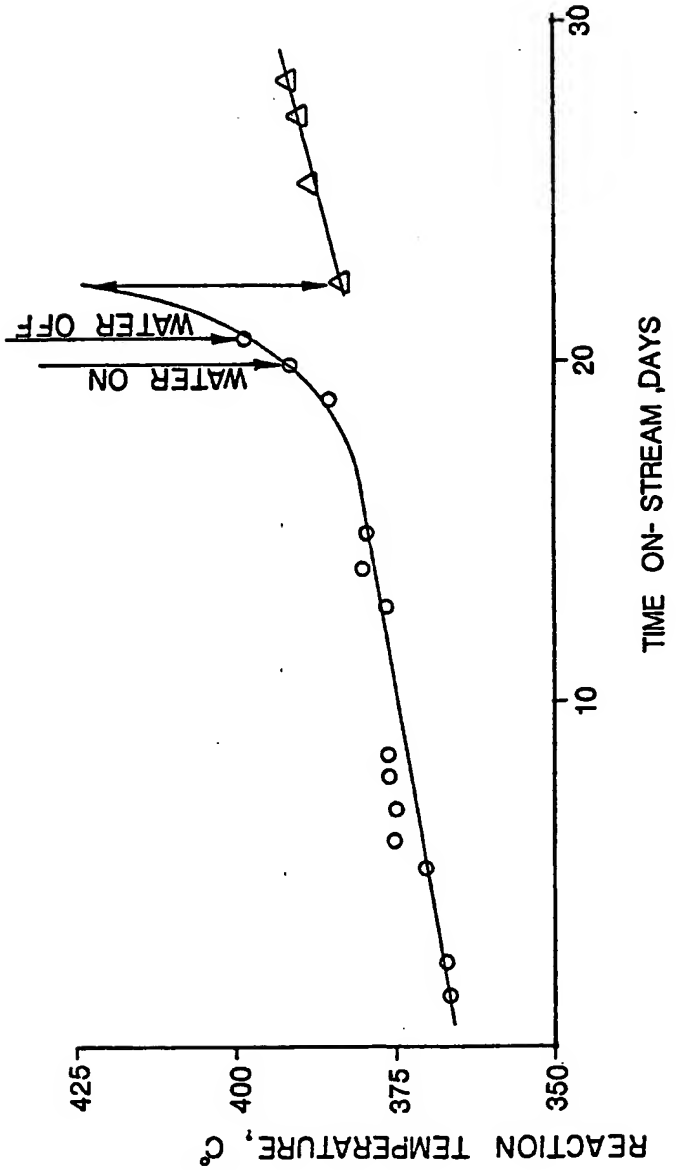
REACTOR
12
2
OIL WELL
24
20
HP SEPARATOR
18
LOW POUR WAXY CRUDE

FIG. 1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375
350
REACTION TEMPERATURE, C°
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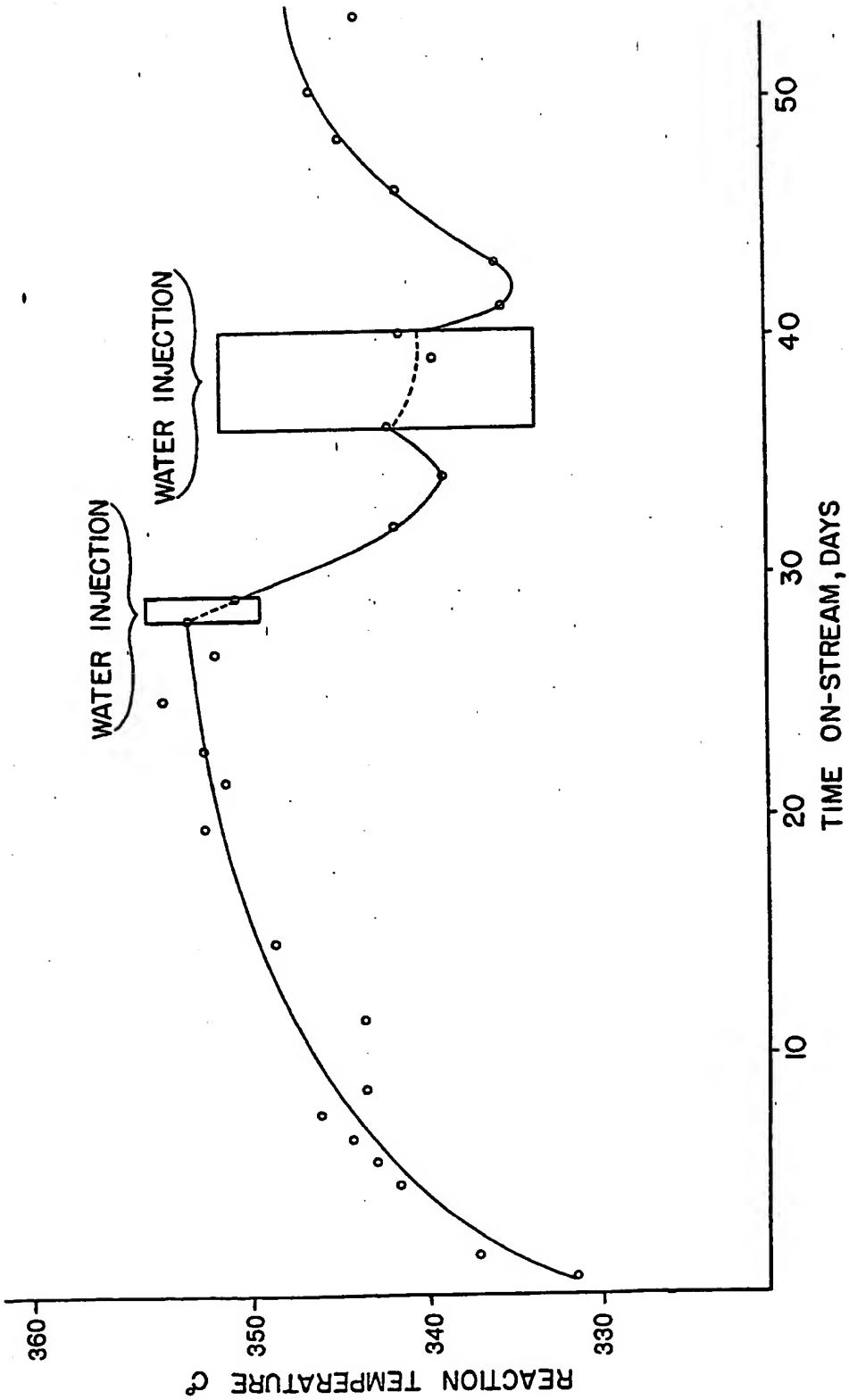
20
30
TIME ON- STREAM ,DAYS

FIG. 2


WATER INJECTION
WATER INJECTION
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10
20
30
40
50
TIME ON-STREAM, DAYS

FIG. 3

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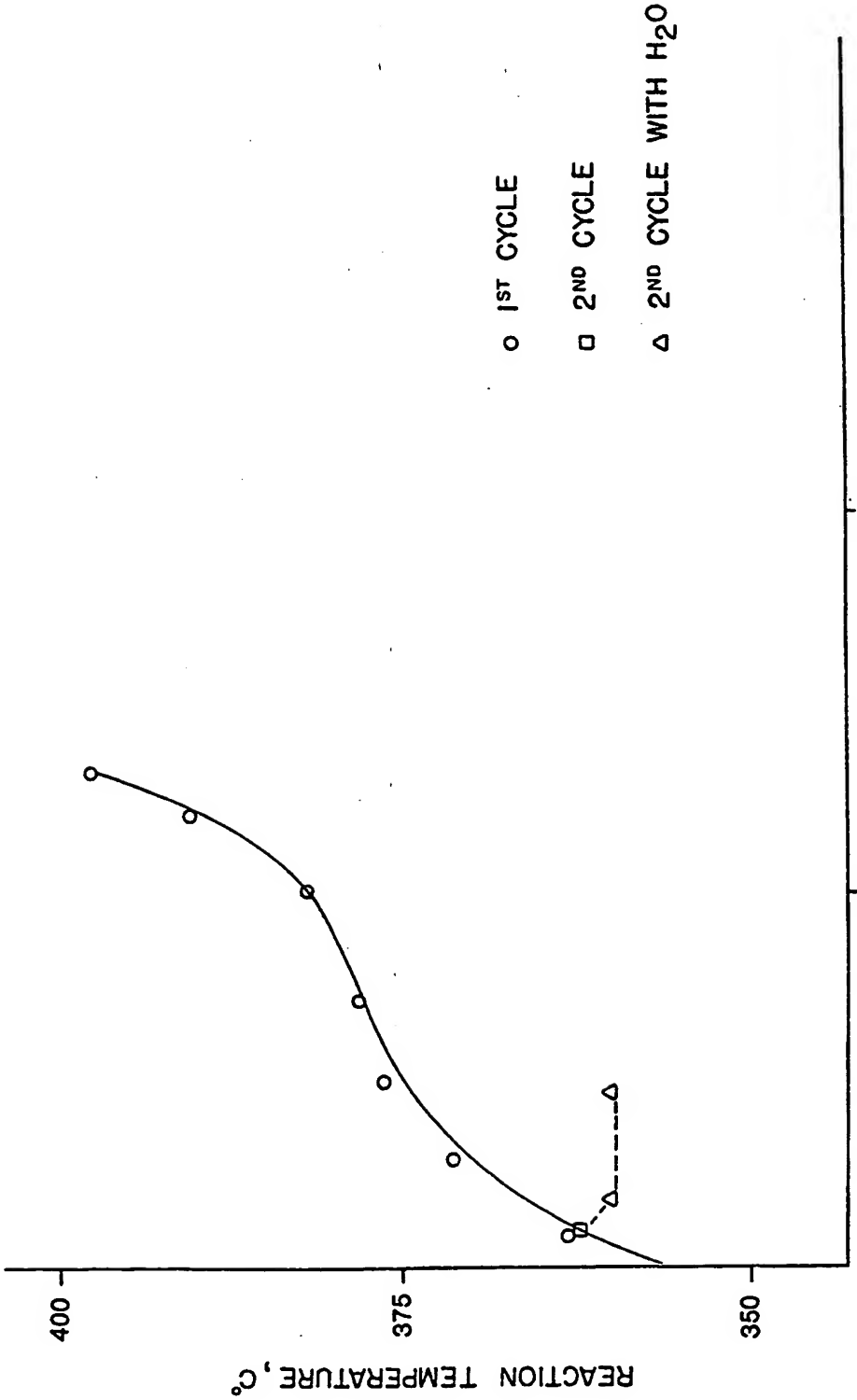



FIG. 4

2109402

FIG. 5

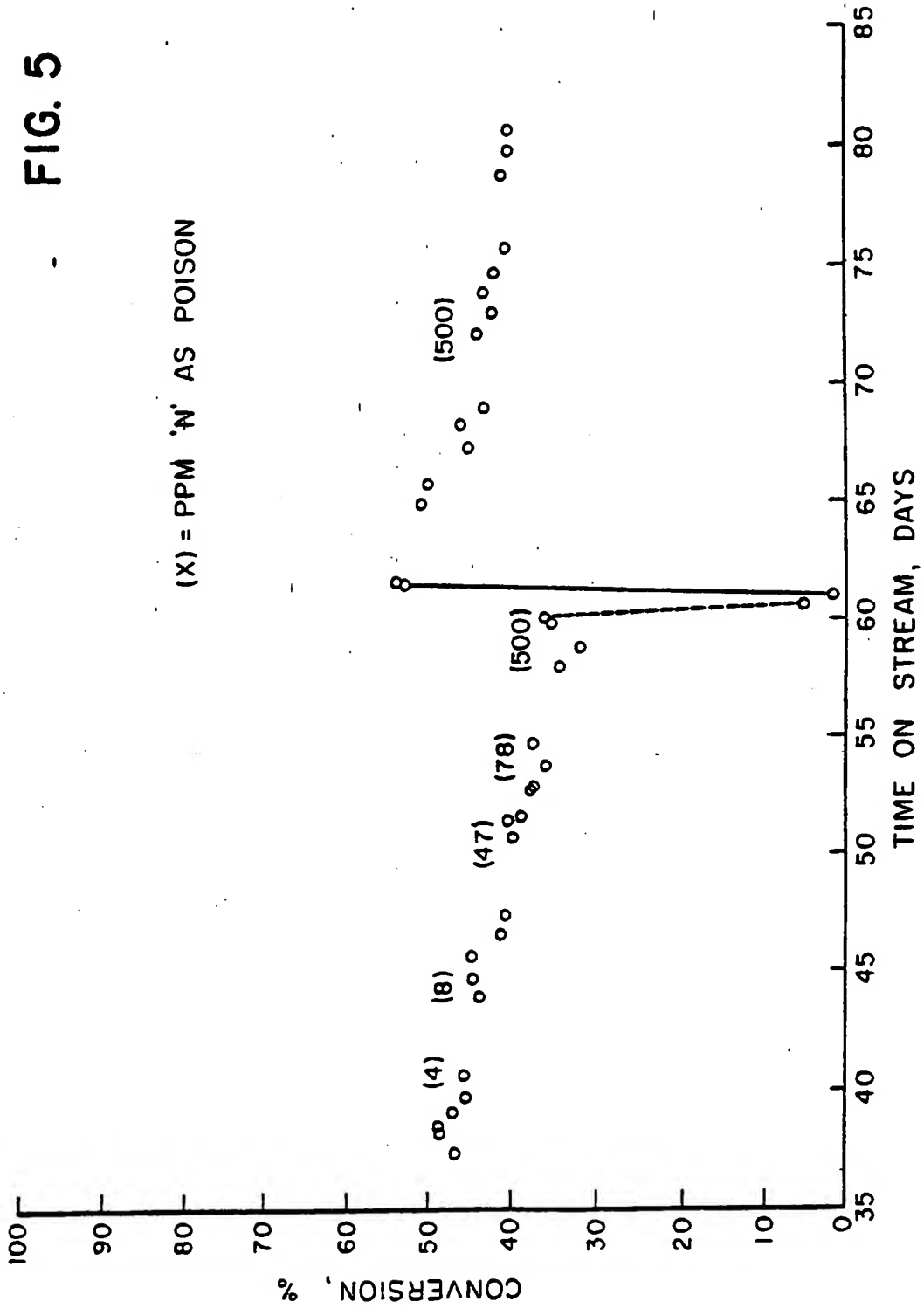
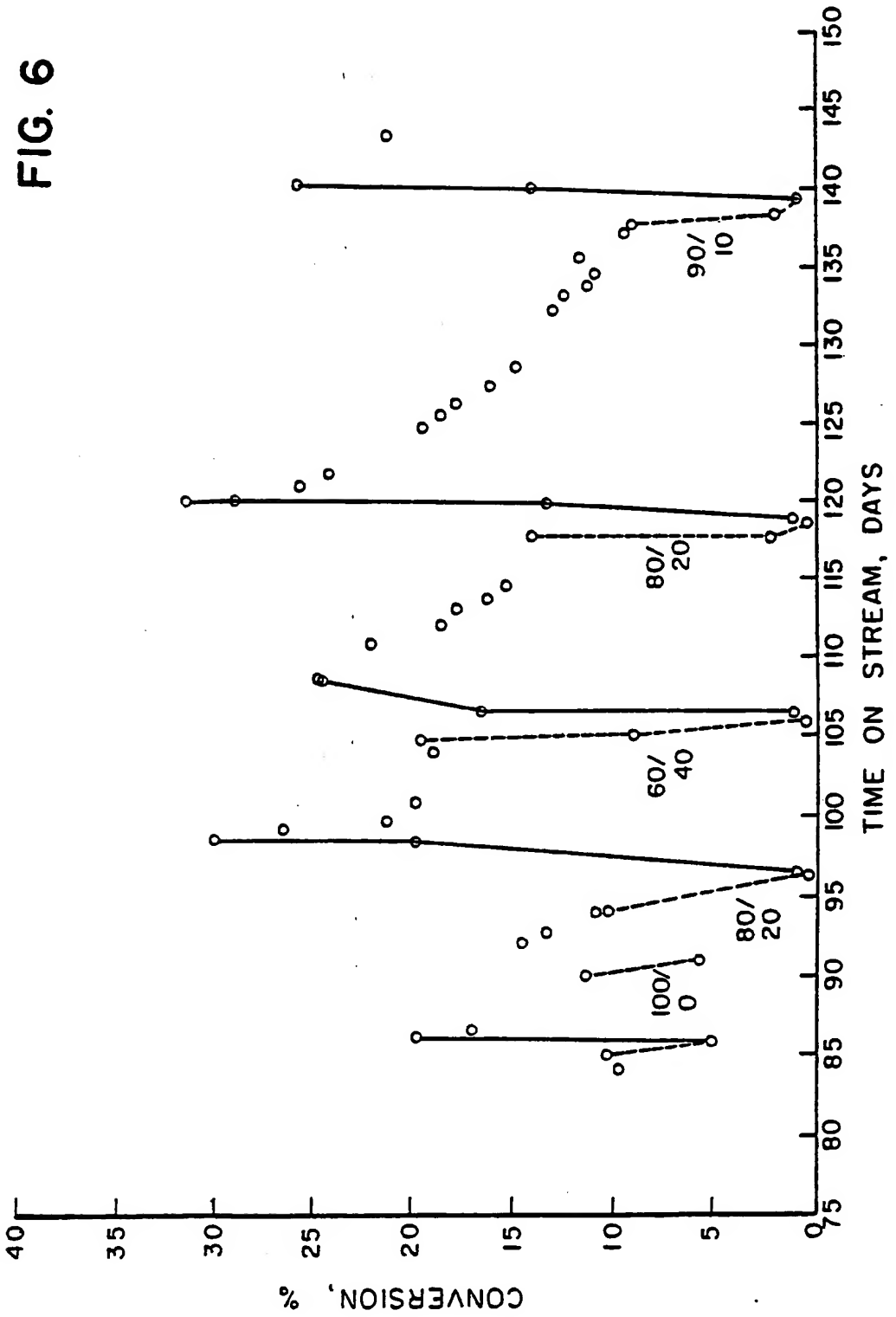


FIG. 6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15
20
25
30
35
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TIME ON STREAM, DAYS
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80
85
90
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100
105
110
115
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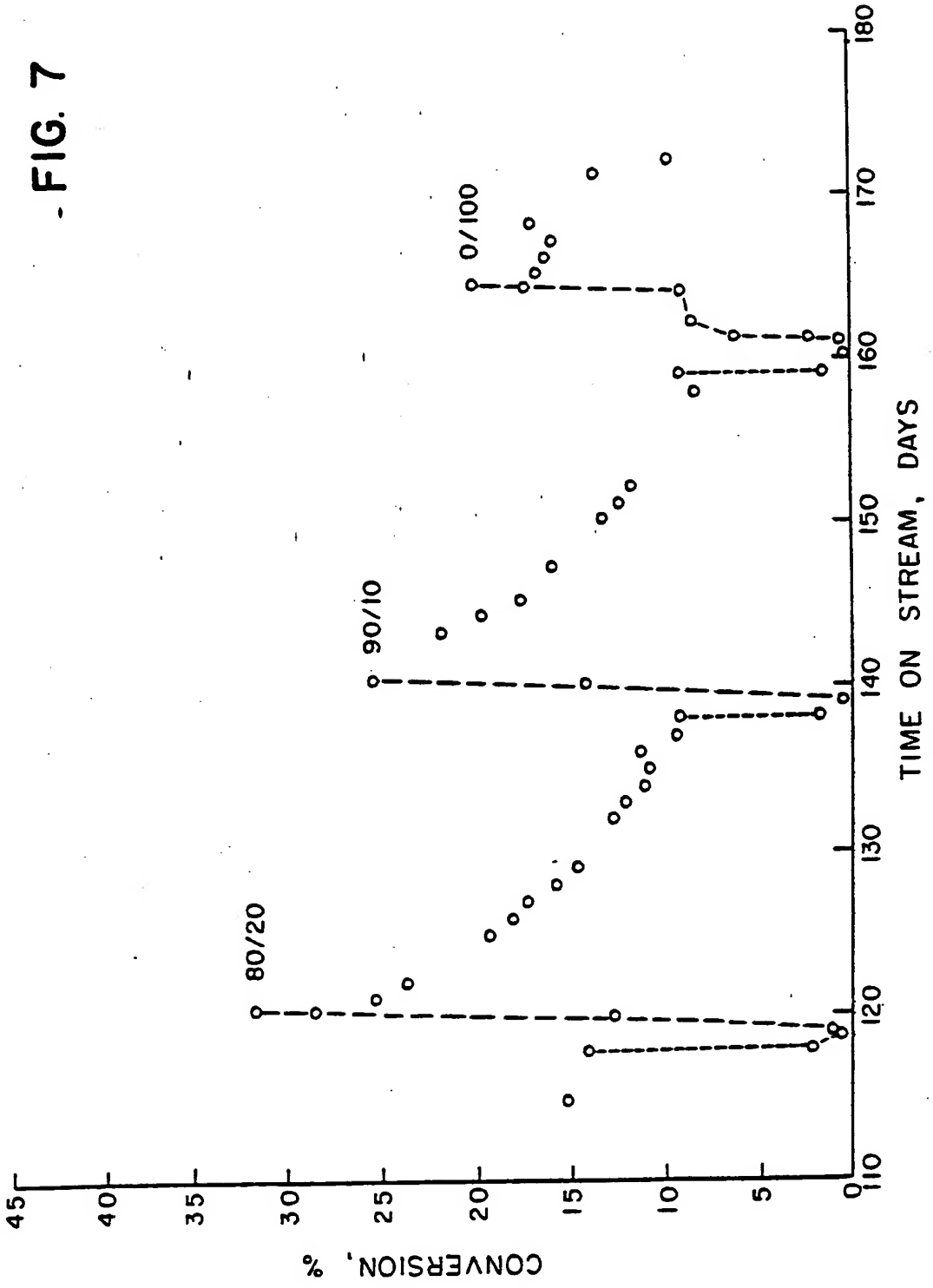
125
130
135
140
145
150
90/10
80/20
60/40
80/20
100/0

FIG. 7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TIME ON STREAM, DAYS
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150
160
170
180
80/20
90/10
0/100

SPECIFICATION

**Method for maintaining activity of zeolite catalysts**

This invention relates to a method for maintaining the activity of zeolite catalysts used in reactions with hydrocarbon feedstocks. The method may be used to prolong the effective life of the catalyst or to rejuvenate or reactivate it.

Catalytic processes are well known in the petroleum refining industry, for example, cracking, hydrocracking, hydrofining, isomerization and dewaxing. The effective life of the catalyst in operations such as these depends on the nature of the feedstock, the severity of the conditions and upon other factors. Often, the activity of the catalyst decreases with time but it is usually possible to compensate for the deactivation by raising the operating temperature.

The activity of certain amorphous and crystalline catalysts depends in part upon the degree of hydration of the catalytic surface. The effect of water on the hydrocracking activity of a palladium-impregnated rare-earth exchanged zeolite X (Pd/REX) and a platinum-impregnated hydrogen zeolite Y (Pt/HY) is described in J. Catalysts *25*, 204-211 (1972). If a controlled amount of water or a water precursor such as 2-pentanol is added to the feed, the activity of the Pd/REX catalyst increases, as shown by a diminution in the equilibrium temperature for a given conversion. If, however, an excessive amount of water is used, the activation may be lost, possibly because of competition between the water and the hydrocarbon for active sites or because of protonic hydration to diminish acidic strength; the effect is, in any event, caused by the water and not by other products of dehydration of the water precursor. On the other hand, water tends to suppress the activity of the Pt/HY catalyst and it is of minimal effectiveness of the hydrocracking of a commercial, low nitrogen feedstock over the Pd/REX catalyst.

The cationic form of the zeolite may require to be appropriately selected for activation to be observed since it has been shown that water may have no effect on the alkali metal forms of the zeolite: J. Catalysis *11*, 238-250 (1968); Soviet Scientific Reviews, Section B, Chemistry Reviews, *2*, 1-6, (1980).

The use of water to enhance the activity of catalysts comprising a metal on an oxide support in petroleum refining processes has been proposed, for example, in U.S. Patent Nos. 2,642,383 and 3,649,524 (reforming), U.S. Patent No. 3,720,602 (hydrodesulfurization), U.S. Patent No. 3,907,921 (dehydrogenation) and U.S. Patent No. 4,097,364 (hydrocracking). Water has also been reported to be useful for promoting the activity of zeolites in these types of process, for example, in U.S. Patent No. 3,493,490 (cracking), U.S. Patent Nos. 3,546,100 and 4,097,364 (hydrocracking) and U.S. Patent No. 4,149,960 (dewaxing).

The present invention is based on the observation that the activity of a zeolite catalyst may be maintained or enhanced by co-feeding water and/or a water precursor such as an alcohol to the reaction zone. The use of the water together with the water precursor is generally found to provide results which are superior to those obtained with water or its precursor alone. An an alternative to the water and/or the water precursor, hydrogen sulfide and/or a precursor of hydrogen sulfide such as a mercaptan may be used although they are somewhat less preferred.

Accordingly, the present invention provides a method for activating a crystalline zeolite catalyst employed in a hydrocarbon conversion process in which a hydrocarbon is contacted with the zeolite under conversion conditions of elevated temperature and pressure, which method comprises contacting the zeolite with (i) water or hydrogen sulfide and/or (ii) a precursor of water or hydrogen sulfide.

The activation procedure of the invention may be used in a wide variety of processes including cracking, hydrocracking, isomerization and dewaxing although greater benefits may be obtained with some processes than others. The zeolites which are most apt to be treated by this procedure are the ZSM-5 type zeolites, especially ZSM-5 itself.

The procedure for maintaining the activity of a zeolite or for enhancing its activity according to the invention will, for convenience, be referred to as an activation process. It may be used with the crystalline zeolite catalysts, of which many are known. Some occur in nature, for example, mordenite, erionite and ferrierite and others at least so far, are obtainable only by synthesis, for example, zeolites X and Y. The zeolites are characterized by ordered porous structures of varying pore sizes. Zeolites such as faujasite, zeolite X and zeolite Y with pore sizes over 6 A are generally regarded as large pore zeolites; these zeolites permit relatively unrestrained access by molecules of various sizes to their internal structure. The small pore zeolites, on the other hand, such as erionite and zeolite A, with pores about 4 A in size, provide highly restrained access to their internal pore structure. The zeolites which benefit the most from the present activation process are those which provide constrained access for larger molecules to their internal structure. This access is conveniently measured by the Constraint Index of the zeolite. The method by which the Constraint Index is measured is described in U.S. Patent No. 4,016,218 and J. Catalysis *67* 218-222 (1981), to which reference is made for details of the method and for examples of the values of the Constraint Index for typical zeolites. The zeolites which are preferably used in the present process have a Constraint Index of 1 to 12 and, in addition, a silica:alumina ratio of at least 12. Zeolites of this type include ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38. These zeolites are described, respectively, in U.S Patent Nos. 3,702,886, 3,709,979, 3,832,449, 4,016,246 and 4,046,859 and reference is made to these patents for details of these zeolites and their preparation. Highly siliceous forms of ZSM-5 are described in U.S. Patent No. Re 29,948 and highly siliceous forms of ZSM-11 and ZSM-12 in published European Patent Applications 14059 and 13630.

Other zeolites may also be treated by the present activation procedure, especially the large pore zeolites such as zeolite Y, especially in its ultrastable

form USY, zeolite beta and ZSM-20. Small pore zeolites may also be treated but it should be remembered that whatever zeolite is selected should be resistant to the effects of water under the reaction conditions used. Thus, if water is known to cause the collapse of a zeolite, this zeolite should not be used. Zeolite beta is described in U.S. Patent Nos. 3,308,069 and Re 28,341 ZSM-20 in U.S. Patent Nos. 3,972,983 and 4,0121,331 and USY in U.S. Patent Nos. 3,293,192 and 3,402,996. For these zeolites, silica:alumina ratios of at least 12 and preferably higher, are also preferred.

The effect of the activation procedure is most notable when the zeolite is wholly or substantially in the alkali metal exchanged form, especially the sodium form, although improvements in its activity may also be noted when the zeolite is only partly in the alkali metal form, for example in the H/Na form. The zeolite may be also be in the rare earth form although this will be less preferred than the alkali metal form. The cationic form of the zeolite may be changed by conventional exchange techniques including base exchange to the ammonium form followed by calcination to give the hydrogen form of the zeolite.

The zeolite is preferably used in a low acidity form having an alpha value of less than 10, preferably less than 5. The method by which alpha is determined is described in U.S. Patent No. 4,016,218 and J. Catalysis, VI, 278-287 (1966). The zeolite may be converted from high acidity forms to the desired low acidity form by the various techniques well known in the art. Briefly, the zeolite which usually has an alpha value of 20 or more, is steamed to reduce the initial acidity after which the steamed zeolite is base exchanged with alkali metal cations to reduce its acidity still further. During the steaming the alpha value will be reduced and normally the steaming should be continued until alpha is reduced by at least about 10 units, normally to a value of at least 10. Base exchange with the alkali metal cations will then reduce alpha to the desired final value of less than 10. Steaming is conveniently carried out at temperatures from 200°C to 700°C, more usually 300°C to 600°C, and for a period of time from about 2 to 48 hours. The atmosphere may be wholly or partly of steam and if another gas is present in addition to the water vapor it should preferably be an inert gas such as nitrogen, especially at the higher steaming temperatures. The subsequent base exchange with alkali metal cations such as sodium, potassium or lithium will substantially reduce the activity of the zeolite for n-hexane cracking. Although catalysts with alpha values below 0.5 may still exhibit some n-hexane cracking activity, this residual activity will be so small that the zeolite can be regarded as inactive.

The desired low acidity may also be obtained by using highly siliceous zeolites such as those described in U.S. Patent No. Re. 29,948 since these high silica materials have a lower intrinsic acidity because the number of active aluminum sites is reduced. These zeolites too, may be subjected to steaming and base exchange to reduce their acidity to the desired low values, with alpha below 10 and preferably below 5. Typical silica:alumina ratios for these highly siliceous zeolites are from 50:1 and higher, especially from 70:1 and higher. Ratios may be very high, for example, above 1000:1, for example 1600:1 or even higher for example 50,000:1. The silica:alumina ratio referred to in this context are the structural or framework ratios, that is, the ratio for the $SiO_4$ to the $AlO_4$ tetrahedra which together constitute the structure of which the zeolite is composed. This ratio may vary from the silica:alumina ratio determined by various physical and chemical methods. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite, thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain treatments such as the dealuminization methods described below which result in the presence of ionic aluminum free of the zeolite structure are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined.

The alkali metal content of the zeolite will vary inversely with the structural silica:alumina ratio because it is the aluminum atoms in the framework which provide anionic sites which accept the alkali metal cations. If the zeolite has been steamed and base exchanged to reduce its acidity, the structural aluminum content will be modified to a certain degree and the final alkali metal content correspondingly reduced.

The activation process of the invention may be used in a variety of hydrocarbon conversion processes but it is particularly applicable to cracking and hydrocracking processes and also to processes which employ the reactions characteristic of cracking and hydrocracking, for example, dewaxing (which, as generally practiced, is a shape selective hydrocracking reaction) and hydrotreating (which involves some cracking of heterocyclics in order to convert the heterocyclic atoms such as nitrogen and sulfur to hydrogenated forms such as ammonia and hydrogen sulfides). The process is particularly useful in catalytic dewaxing processes which are normally carried out in the presence of hydrogen and are therefore correctly referred to as hydrodewaxing processes. In processes of this kind, the waxy constituents of the feedstock, which are long chain, for example $C_{12}+$, normal paraffins are converted to shorter-chain fragments which do not make so great a contribution to high pour points in the product. The hydrogen, besides its function of hydrogenating some unsaturated bonds in the feedstock contributes to this reaction mainly by preventing the catalyst from aging prematurely although if the conditions are appropriate, cracking and hydrogenation of polycyclic aromatics in the feedstock may occur. Catalytic dewaxing processes of this kind which may employ the present activation process as an adjunct are described, for example, in U.S. Patent Nos. 3,668,113, 3,894,938, 4,176,050, 4,181,598, 4,222,855,

4,229,484 and 4,247,388 and reference is made to these patents for details of the operating conditions employed in processes of this kind. Dewaxing processes using the present activation procedure may be carried out in the presence or absence of hydrogen and in the presence or absence of added gas other than hydrogen. It is generally preferred, however, that such processes are carried out with added gas, either hydrogen or $C_1$-$C_3$ hydrocarbons such as methane.

The procedure of the invention may also be applied to crude oil dewaxing processes. Since gaseous hydrocarbons such as methane are often associated with crude oil deposits, such crude oil dewaxing processes may advantageously be carried out, especially on-site at the well head, in the presence of such methane. Such a process is described in more detail below with reference to Figure 1 of the accompanying drawings.

The reaction conditions employed will be those appropriate to the reaction in question. Thus, if the process is catalytic dewaxing, the temperatures will generally be from 300°C to 500°C at pressures of 5000 kPa or greater with hydrocarbon space velocities of 0.1 to 20, more usually 0.2 to 5. Hydrogen circulation rates from 200 to 1000 n.1.1.$^{-1}$ (liters of hydrogen – measured at standard temperature and pressure – per liter of oil feedstock) will normally be employed.

The activation process will not generally be required with the conventional kinds of cracking such as fluid catalytic cracking because these reactions are normally carried out at high temperatures for example above 450°C with continuous regeneration of the catalyst. At these high temperatures, any nitrogen compounds with which the zeolite comes into contact will be desorbed and therefore will not remain to reduce catalytic activity. In addition, the rate of coke formation at these higher temperatures is so fast that continuous regeneration is necessary and, in which case, the theoretical possibility of an extended duration between successive regenerations is of no moment. However, the activation process will be of use with low temperature cracking and other reaction which are carried out at lower temperatures and where some cracking reactions do take place, for example, in hydrocracking where extended duration between regeneration would be useful.

Hydrocracking normally employs temperatures below 450°C because the thermodynamics of the process become unfavorable at higher temperatures; temperatures of 350°C to 400°C are common at pressures above 10,000 kPa with hydrogen circulation rates of 200 to 1000n.1.1.$^{-1}$ of hydrogen feed at a space velocity of 0.1 to 20, more usually 0.2 to 5. In all processes, conditions may be varied in order to compensate for catalyst aging and other variations, as is conventional.

The feedstocks which are used are those appropriate for the process in question and may typically range from naphthas, through light and heavy distillates such as kerosenes, jet fuels and light gas oils to heavy oils boiling above about 340°C, for example, whole crudes, reduced crudes (vacuum and atmospheric), heavy gas oils, coker gas oils, FCC tower bottoms and oils derived from shale, tar sands and coal.

The process is carried out in a manner appropriate to its nature. For example, hydrocracking may be carried out in a fixed bed downflow trickle type reactor and dewaxing in a similar manner, as is conventional.

If a hydrogenation component is required in the catalyst, it will generally be chosen from the noble metals of Group VIIIA or the non-noble metals of Groups VIA and VIIIA of the Periodic Table. Platinum and palladium are the preferred noble metals and nickel, cobalt, vanadium, molybdenum, chronium and tungsten the preferred base metals. Combinations of the base metals such as cobalt-molybdenum, nickel-tungsten and nickel-tungsten-titanium have been found to give good performance as hydrogenation components. Base metal components may be subjected to pre-sulfidation by a sulfur-containing gas, usually hydrogen sulfide in the presence of hydrogen at an elevated temperature, as is conventional. The metal may be introduced into the catalyst (zeolite, matrix or both) by impregnation, cation exchange or anion exchange using ions such as the complex cations e.g. $Pt(NH_3)_6^{2+}$ or the complex anions such as vanadate, orthotungstate or molybdate, as is conventional.

The zeolite may be incorporated into a binder such as silica, alumina, silica-alumina or silica-magnesia or a matrix such as a clay in order to confer adequate mechanical properties such as attrition and crushing resistance. U.S. Patent No. 4,016,218 describes details of other binders and matrix materials.

The improvement in catalytic activity is achieved according to the invention by injection water and/or a water precursor into the reaction zone. Suitable water precursors include alcohols such as methanol, ethanol, propanol, butanol and higher alcohols, particularly the alkanols, especially 2-pentanol which is easily converted to penetene and water. The water and/or the precursor can be injected in either liquid or gaseous form and can be supplied directly to the conversion reactor or combined with the feed. The addition can be made in a pulsed fashion or continuously. One convenient means is to supply the water or precursor for a prolonged period of time, say, for 8-10 hours while monitoring the reaction temperature necessary to maintain the desired conversion conditions. The addition will usually permit a reduction in the reaction temperature. When periodic additions are employed, it has been found that about 0.01 to about 30 volumes of water-water precursor per unit volume of catalyst are effective for prolonging the catalyst life. The amount of water as such together with the water yielded by the precursor should be so adjusted. These additions may be continued for 6-24 hours or longer. The amount of water precursor will, of course, be dependent on the particular material employed and the amount of water the selected precursor produces. It is possible to add the water, water precursor or mixture to the feed or the reactor continuously in a manner which will maintain the desired operating conditions but this will normally not be preferred because the conver-

sion will often decrease during the time that the addition is being made. Normally, the addition of the water and/or water precursor will be used to reduce the operating temperature of the process for example to maintain the operating temperature at the value used at the start of the operating cycle.

The use of water together with the water precursor generally produces notable advantages over the use of either material on its own. The degree of activation produced by the mixture is generally greater than that produced by the water or water precursor alone in corresponding amounts and accordingly, it is possible to obtain relatively greater improvements in operating conditions for example lower temperatures for a given amount of activator required to produce a given amelioration of operating parameters. When both water and water precursor are used together, the weight ratio between the water and the precursor will normally be fromm 10:90 to 90:10 and more usually from 25:75 to 75:25. Equal proportions by weight have been shown to give good results.

The amount of water and/or precursor which will be used will normally be in the range of 0.1 to 20 volume percent of the feed, preferably 1 to 10 volume percent, calculated where appropriate as the combined volume of water and water precursor with the ratio between them being varied in the manner previously described. When continuous addition of water and/or water precursor is used, addition of less than 5 volume percent has been found to be especially useful.

As an alternative to water, hydrogen sulfide may be used and, as an alternative to the water precursor, a hydrogen sulfide precursor such as a mercaptan for example propyl mercaptan, although these materials will normally be less preferred than water, water precursor or water/water precursor combination. The mercaptan may be used in amounts similar to those used for the water precursor but normally the amount of hydrogen sulfide should not exceed 10 volume percent of the feed because of equipment corrosion problems which tend to arise with greater amounts. Otherwise, similar amounts and proportions may be used.

As mentioned above, the procedure of the invention may be applied to crude oil dewaxing. In fact, the invention is especially applicable to such processes carried out at the wellhead since the catalyst may contain no hydrogenation metal and the lack of availability of hydrogen in the field for use in the dewaxing process is therefore of no great consequence; waxy crudes are generally low in sulfur and metal contaminants; and the hydrocarbon gases associated with the crude oil can be used to pressurize the dewaxing system.

Figure 1 of the accompanying drawings illustrates schematically a process for carrying out wellhead dewaxing utilizing the procedure of the invention.

Referring to Figure 1, a waxy crude oil together with gaseous hydrocarbons from a producing well 2 pass at formation temperature through line 4 to pump 6 which discharges to the tubes of heat exchanger 8 to be preheated by exchange against the product of the process. The preheated waxy crude passes from heat exchanger 8 to furnace 10 where it is heated further to a temperature suitable for the dewaxing. The heated charge is introduced into reactor 12 for dewaxing in the presence of a presteamed sodium exchanged zeolite catalyst, for example a presteamed NaZSM-5. Water is injected into the system at a convenient point; for example, it can be supplied through line 14 for admixture with the crude in the suction line to pump 6 or through line 16 directly into reactor 12.

Products of the reaction, constituted by low pour point crude with a small amount of gaseous hydrocarbons, are transferred to a high pressure separator 18 from which the low pour point liquid product of the conversion in reactor 12 is transferred by line 20 to the shell side of heat exchanger 8 where it is cooled by supplying heat to the incoming charge as above described. The cooled product flowing through line 22 from the shell side of heat exchanger 8 is a low pour point liquid petroleum suitable for transport by pipeline. Gaseous hydrocarbons of 1-4 carbon atoms are withdrawn from separator 18 and pass through compressor 24 for recycle by line 26 to the heated feed leaving furnace 10. Where additional methane is required in the process it may be provided to the recycle gas stream through line 30.

In the whole crude dewaxing process described above, the temperature of the reaction is suitably from 316 to 460°C, depending on the feed. However, with the particular catalyst utilized herein which is prepared by steaming to an alpha value of not less than 10 followed by base exchange with alkali, satisfactory activity has been achieved at temperatures less than 370°C. Many charge stocks will undergo some thermal cracking at temperatures above about 430°C with resultant production of undesired gaseous hydrocarbons thereby losing one advantage of the invention to the extent that thermal cracking takes place.

Pressures employed will vary according to the technique being used. For liquid full reactor operation, the minimum pressure will be that necessary to maintain the charge in the liquid phase at the temperature of reaction. In any event, the pressure will be above about 1400 kPa. There appears to be no maximum pressure limit imposed by effectiveness of the catalyst, but costs for capital installation and operation of compressors and the like rise rapidly for pressures in excess of 14,000 kPa. When methane or hydrogen or any other gas is added to the system, it is preferred to operate below that level for economic reasons. Gas circulation may be maintained at from 0 to 2700 $n.1.1^{-1}$.

Space velocity will vary somewhat with the type of feed, permitting a higher space velocity for a feedstock which is easily dewaxed. In general, space velocity will range from about 0.1 liquid volume of hydrocarbon charge per volume of catalyst per hour (LHSV) up to about 5.0 LHSV. For most charge stocks, preferable LHSV will range from about 0.3 to 1.0.

The following Examples illustrate the invention. In the Examples, all percentages are by weight unless otherwise stated.

*EXAMPLE I*

A presteamed sodium form of ZSM-5 was prepared as follows:

The ammonium form of ZSM-5 extrudate was contacted with 100% steam at 455°C for 16 hours. The steam treated product was added to 1N $NH_4NO_3$ solution, pH 4. The mixture was maintained at 93°C for 4 hours with continuous stirring, then the liquid was decanted and the catalyst was washed with deionized water. The resulting catalyst was then Na-exchanged (pH of exchange 8-9) to an alpha value of 0.3 by adding 1.0 gram of the treated extrudate (now in the ammonium form) to 60 ml of 0.3 N $NaHCO_3$ solution having a pH of 8.5. The mixture was maintained at room temperature for 3 hours with occasional agitation by swirling or stirring. The liquid was then decanted and replaced with 60 ml of fresh 0.3 N $NaHCO_3$ solution. The sodium exchange was completed in an additional 3 hours. The recovered NaZSM-5 was washed with copious quantities of deionized water (adjusted to a pH of 8-9 with NaOH) and dried at 130°C.

Altamont crude was processed over the recovered catalyst at 343-393°C, 1 LHSV and in the absence of added gas. A continuous run was made with the Altamont crude oil over the presteamed NaZSM-5 extrudate for 28 days. After 20 days water was co-fed at a rate of 5 vol. % of the hydrocarbon feed rate and was maintained for 20 hours only. This pulsed introduction of water during the experiment led to an increase in catalyst activity with time. This increase in catalyst activity corresponding to approximately 17°C reactor temperature. The operating conditions and conversion data for this run are shown in Table 1. The aging curve is shown in Figure 2. The reactor temperature shown in the graph was corrected to yield a total liquid product (TLP) pour point of −1°C using the assumed relationship of +1°C reactor temperature = −2°C of product pour point. It is clear from Figure 2 that water injection improved catalyst activity and the reactor temperature required for −1°C pour point liquid product was lowered by 17°C. Translating this temperature improvement to cycle life corresponds to an additional week in the length of the cycle. This pulsed water injection can be repeated and the catalyst life cycle can be extended.

TABLE 1 PROCESSING OF ALTAMONT CRUDE OVER PRESTEAMED NaZSM-5

| Time on Stream (days) | | 1 | 1.5 | 2.5 | 5.3 | 6.1 | 6.9 | 7.9 | 8.9 | 12.9 | 13.9 | 14.9 | 16 | 19 | 20 | 20.7 | 22.5 | 25.5 | 27.5 | 28.2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| System Pressure (kPa) | | 2240 | 2240 | 2240 | 2200 | 2310 | 3410 | 2340 | 2270 | 2240 | 2200 | 2170 | 2170 | 2240 | 2340 | 2240 | 2340 | 2310 | 2310 | 2170 |
| Reaction Temp., °C | | 343 | 371 | 371 | 371 | 371 | 371 | 377 | 377 | 377 | 377 | 377 | 382 | 382 | 382 | 382 | 388 | 388 | 388 | 393 |
| LHSV | | 0.9 | 0.87 | 0.6 | 1.24 | 1.18 | – | 1.12 | 1.00 | 0.65 | 1.11 | 0.89 | 1.22 | 1.10 | 1.18 | 1.09 | 1.12 | 1.11 | 0.81 | .7 |
| H2O Feed Rate cc/hrs | | – | – | – | – | – | – | – | – | – | – | – | – | – | – | 0.4 | – | – | – | – |
| *Yield Wt.* | | | | | | | | | | | | | | | | | | | | |
| Methane | | – | .01 | .02 | .01 | .01 | – | .02 | .02 | .04 | – | – | .01 | .02 | .02 | .01 | .03 | .03 | .01 | .04 |
| Ethane | | – | .02 | .04 | .02 | .01 | – | .04 | .04 | .04 | – | – | .02 | .04 | .04 | .02 | .08 | .07 | .03 | .01 |
| Ethene | | – | .03 | .04 | .04 | .01 | – | .09 | .07 | .09 | – | – | .03 | .09 | .08 | .05 | .13 | .13 | .05 | .14 |
| Propane | | – | 1.16 | 1.88 | 1.11 | .44 | – | 1.73 | 1.76 | 1.52 | – | – | .06 | 1.69 | 1.50 | .99 | 2.17 | 1.82 | 1.03 | 2.60 |
| Propene | | – | .18 | .27 | .35 | .13 | – | .57 | .54 | .45 | – | – | .24 | .66 | .68 | .79 | .80 | .79 | .40 | .98 |
| Isobutane | | – | 1.21 | 2.15 | .83 | .45 | – | 1.19 | 1.38 | 1.24 | – | – | .40 | 1.12 | 1.01 | .58 | 2.06 | 1.11 | .81 | 1.85 |
| n-Butane | | – | 1.09 | 2.17 | .91 | .60 | – | 1.30 | 1.44 | 1.38 | – | – | .49 | 1.13 | 1.25 | .77 | 2.18 | 1.33 | 1.12 | 2.07 |
| t-butene | | – | .04 | .08 | .08 | .05 | – | .11 | .12 | .11 | – | – | .05 | .17 | .17 | 0.19 | .19 | .17 | .14 | .25 |
| Isobutene | | – | .16 | .33 | .35 | .21 | – | .51 | .57 | .50 | – | – | .24 | .66 | .70 | 0.73 | .77 | .66 | .54 | 1.00 |
| Trans-2-Butene | | – | .04 | .09 | .09 | .06 | – | .14 | .15 | .13 | – | – | .07 | .19 | .20 | 0.22 | .24 | .20 | .19 | .30 |
| Cis-2-Butene | | – | .04 | .09 | .09 | .06 | – | .14 | .15 | .13 | – | – | .07 | .19 | .20 | 0.22 | .24 | .20 | .19 | .30 |
| Total Gas (C4–) | | – | 3.9 | 7.2 | 3.9 | 2.0 | – | 5.85 | 6.2 | 5.8 | – | – | 2.2 | 6.0 | 5.9 | 4.6 | 9.4 | 6.5 | 4.6 | 9.6 |
| | *Feed* | | | | | | | | | | | | | | | | | | | |
| C5-166°C | 6 | | | | 32.2 | | – | 38.2 | 31.8 | – | – | – | – | 30.5 | – | – | 28.9 | 32.5 | – | – |
| 166°C-427°C | 45 | | | | 36.0 | | – | 34.0 | 33.6 | – | – | – | – | 34.8 | – | – | 30.7 | 31.5 | – | – |
| 427°C | 49 | | | | 28.8 | | – | 23.8 | 29.0 | – | – | – | – | 28.9 | – | – | 31.0 | 29.5 | – | – |
| *Pour Point,* °C | | 32 | –9 | –9 | –1 | 7 | 7 | –1 | –1 | –7 | 7 | 4 | 10 | 7 | 18 | 29 | –7 | 2 | 4 | 2 |
| As drained (RD) | | – | – | – | –4 | – | – | –6 | | –23 | – | – | – | –7 | – | – | –29 | –9 | – | – |
| 166°C-443°C | | – | – | – | 49 | – | – | 49 | | 49 | – | – | – | 49 | – | – | 49 | 49 | – | – |
| 454°C+ | | – | – | – | 78.9 | – | – | 79.1 | | 80.4 | – | – | – | 81.6 | – | – | – | – | – | – |
| Octane – C5 – 166°C | | | | | | | | | | | | | | | | | | | | |

*EXAMPLE II*

A presteamed NaZSM-5 catalyst was prepared by contacting $HN_4ZSM$-5 extrudate with 100% steam at 455°C for 15 hours. As in Example I, the steam treated product was treated with 1N, $NH_4NO_3$ and washed with deionized water. The resulting product was then nitrogen calcined at a rate of 1°C/min to 538°C for 4 hours. As in Example I, the nitrogen calcined catalyst was sodium exchanged to an alpha value of 0.3.

A continuous run of 53 days was used to process Gippsland whole crude over the resulting catalyst in the presence of added methane. The operating conditions and conversion data for this run are summarized in Table 2. Gippsland crude, pour point 16°C, was readily dewaxed over presteamed NaZSM-5 in the presence of added methane flow. Pour points of TLP ranged from –65 to –32°C. The aging curve and the effect of water injection is shown in Figure 3, where the reaction temperature has been normalized to a total liquid product pour point of –40°C. Co-feeding water at a rate of 5 vol. % of the hydrocarbon feed increased catalyst activity. This increased activity lasted even after the termination of the water injection. The effect of water is reversible as shown in Figure 3. The promotional effect of water reached a maximum and this maximum roughly corresponded to the beginning of the starting cycle. Soon after catalyst activation, the catalyst behaved as if it were a fresh catalyst.

TABLE 2 PROCESSING OF GIPPSLAND CRUDE OVER PRESTEAMED NaZSM-5

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time on Stream (days) | | 0.9 | 1.8 | 4.8 | 5.8 | 6.7 | 7.7 | 8.7 | 11.7 | 14.8 | 19.6 | 21.6 | 22.9 | 25 | 26.8 | 28 | 29 | 32 |
| System Pressure (kPa) | | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 | 2170 |
| Reaction Temp., °C | | 343 | 343 | 343 | 343 | 343 | 343 | 343 | 343 | 350 | 350 | 350 | 350 | 350 | 354 | 354 | 354 | 354 |
| CH4 rate, cc/min | | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 |
| LHSV | | 0.94 | 1.10 | 1.08 | 1.00 | 0.99 | – | 1.04 | .87 | .84 | .85 | .84 | .76 | .89 | .87 | .88 | .88 | .86 |
| H2O Rate cc/hr | | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | 0.3 | – |
| *Yield, wt.* | | | | | | | | | | | | | | | | | | |
| Methane | | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| Ethane | | .12 | .10 | .14 | .11 | .11 | .14 | .10 | .12 | .11 | .13 | .08 | .08 | .08 | .08 | .08 | .06 | .09 |
| Ethene | | .07 | .05 | .06 | .05 | .05 | .04 | .04 | .04 | .05 | .04 | .03 | .04 | .04 | .05 | .05 | .07 | .10 |
| Propane | | 1.29 | 1.03 | 1.06 | .90 | .87 | .98 | .75 | .84 | .85 | .83 | .73 | .79 | .81 | 1.00 | .96 | 1.15 | 1.32 |
| Propene | | .50 | .51 | .68 | .62 | .62 | .68 | .51 | .62 | .65 | .73 | .65 | .66 | .74 | .79 | .76 | .47 | .76 |
| Isobutane | | 1.52 | 1.03 | .84 | .75 | .71 | .81 | .63 | .62 | .65 | .61 | .52 | .61 | .58 | .80 | .77 | 1.25 | 1.22 |
| n-Butane | | 2.71 | 2.25 | 1.91 | 2.05 | 1.99 | 2.44 | 1.73 | 1.68 | 1.70 | 1.84 | 1.54 | 1.85 | 1.78 | 2.17 | 2.08 | 2.16 | 2.44 |
| I-Butene | | .16 | .13 | .16 | .20 | .21 | .21 | .17 | .19 | .21 | .23 | .21 | .21 | .23 | .25 | .25 | .15 | .24 |
| Isobutene | | 2.64 | 2.16 | 1.40 | .90 | .90 | .81 | .78 | .79 | .87 | .98 | .88 | .91 | 1.00 | 1.14 | 1.07 | .68 | 1.02 |
| Trans-2-Butene | | .51 | .49 | .41 | .63 | .56 | .56 | .49 | .43 | .46 | .62 | .54 | .56 | .62 | .67 | .65 | .40 | .63 |
| Cis-2-Butene | | .31 | .31 | .25 | .39 | .38 | .38 | .33 | .29 | .31 | .42 | .36 | .38 | .42 | .45 | .44 | .27 | .38 |
| | *Feed* | | | | | | | | | | | | | | | | | |
| Total Gas (C4) | | 9.8 | 8.1 | 6.9 | 6.6 | 6.4 | 7.1 | 5.5 | 5.6 | 5.9 | 6.4 | 5.6 | 6.1 | 6.3 | 7.4 | 7.1 | 6.7 | 8.2 |
| C5-166°C (est) | 37 | 48.5 | 48.1 | 41.5 | 45.6 | 51.8 | 46.9 | 51.4 | 49.7 | 49.0 | 51.6 | 49.5 | 48.4 | 46.1 | 50.5 | 56.9 | 48.3 | 60.8 |
| 166°C-427°C (est) | 53 | 35.6 | 35.7 | 43.2 | 40.8 | 35.2 | 38.7 | 35.8 | 42.3 | 40.5 | 38.3 | 37.6 | 38.7 | 41.5 | 37.1 | 31.8 | 37.8 | 27.6 |
| 427°C (est) | 10 | 6.1 | 8.1 | 8.3 | 7.0 | 6.6 | 7.3 | 7.3 | 2.4 | 4.6 | 3.7 | 7.3 | 6.8 | 6.1 | 5.0 | 4.1 | 7.2 | 2.3 |
| *Pour Point, °C* | | | | | | | | | | | | | | | | | | |
| As drained | 16 | –65 | –54 | –43 | –40 | –34 | –34 | –40 | –40 | –43 | –37 | –37 | –37 | –32 | –46 | –43 | –48 | –65 |
| 166°C-427°C | 18 | | | –26 | | | | | 21 | | | | | | | | | |
| 443°C+ | 43 | | | | | | | | 21 | | | | | | | | | |
| Octane C5-166°C | 60 | | | | 68.8 | | | | | | | | | | | | | |

TABLE 2 PROCESSING OF GIPPSLAND CRUDE OVER PRESTEAMED NaZSM-5 (CONTINUED)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Time on Stream (days) | 34.1 | 36 | 39 | 40 | 41 | 43 | 46 | 48.1 | 50.1 | 53 |
| System Pressure (kPa) | 2135 | 2170 | 2170 | 2170 | 2170 | 2170 | 2310 | 2310 | 2310 | 2310 |
| Reaction Temp., °C | 343 | 343 | 343 | 343 | 343 | 332 | 338 | 343 | 343 | 343 |
| CH4 rate, cc/min. | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 |
| LHSV | .87 | .84 | .87 | .87 | .87 | .86 | .87 | .87 | .87 | .89 |
| H2O Rate cc/hr | – | – | 0.3 | 0.3 | – | – | – | – | – | – |
| *Yield, wt.* | | | | | | | | | | |
| Methane | .08 | .08 | .08 | .08 | .08 | .08 | .08 | .07 | .07 | .07 |
| Ethane | .06 | .05 | .06 | .07 | .05 | .03 | .04 | .04 | .04 | .03 |
| Ethene | .99 | .98 | 1.03 | 1.06 | .78 | .66 | .76 | .78 | .75 | .66 |
| Propane | .69 | .69 | .58 | .60 | .48 | .45 | .52 | .54 | .54 | .51 |
| Propene | .82 | .81 | 1.03 | 1.00 | .71 | .53 | .60 | .61 | .58 | .49 |
| Isobutane | 2.17 | 2.21 | 2.27 | 2.14 | 1.61 | 1.67 | .182 | 1.80 | 1.78 | 1.55 |
| n-Butane | .23 | .23 | .19 | .18 | .14 | .14 | .19 | .18 | .19 | .17 |
| I-Butene | 1.05 | 1.06 | .90 | .86 | .72 | .73 | .80 | .85 | .83 | .72 |
| Isobutene | .62 | .64 | .51 | .48 | .46 | .53 | .54 | .55 | .54 | .48 |
| Trans-2-Butene | .42 | .44 | .34 | .32 | .28 | .32 | .33 | .34 | .33 | .29 |
| Cis-2-Butene | | | | | | | | | | |
| Total Gas (C4) | 7.1 | 7.2 | 7.0 | 6.8 | 5.3 | 5.1 | 5.7 | 5.8 | 5.6 | 5.0 |
| C5-166°C (est) | 50.5 | 52.2 | 46.6 | 52.2 | 47.2 | 44.6 | 44.5 | | | |
| 166°C-427°C (est) | 36.7 | 36.5 | 38.7 | 34.8 | 36.2 | 39.48 | 41.4 | | | |
| 427°C (est) | 5.7 | 4.1 | 6.7 | 5.9 | 11.3 | 10.8 | 8.4 | | | |
| *Pour Point, °C* | | | | | | | | | | |
| As drained | –48 | –43 | –48 | –46 | –57 | –34 | –34 | –37 | –34 | –40 |
| 166°C-427°C | | | | | | | | | | |
| 443°C+ | | | | | | | | | | |
| Octane C5-166°C | | | | | | | | | | |

*EXAMPLE III*

A 340°C+ boiling point fraction of Minas crude, pour point of 46°C, was processed over the catalyst of Example II. The feed was passed over the catalyst at temperatures of 360-388°C, 0.9 LHSV and in the presence of added methane. A dewaxed liquid product with 16°C pour point was obtained over a cycle length of 10 days. At the conclusion of the first cycle, the catalyst was air regenerated and a second pretopped Minas crude cycle was begun. The results of the first day of the second cycle with the regenerated catalyst were identical to the first cycle results obtained with the fresh catalyst. After the first day water was co-fed at a rate of 3-5 vol.% of the hydrocarbon feed rate, an enhanced state of dewaxing activity was maintained at 0.8 LHSV for the pretopped crude. The operating conditions and results are shown in Table 3 and Figure 4 where the reaction temperature has been normalized to a TLP pour point of 16°C. Figure 4 shows that the benefits of water injection observed in Examples I and II are obtained with a regenerated catslyst even though

water injection was not employed in the first cycle of the fresh presteamed NaZSM-5 catalyst.

*TABLE 3 PROCESSING OF PRETOPPED MINUS CRUDE OVER PRESTEAMED NaZSM-5*

| | | First Cycle | | | | | | | | | | | | Second Cycle | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time on Stream (days) | | 0.9 | 2.9 | 5 | 7.1 | 10 | 12 | 13 | 14 | 17 | 18 | 19 | 20 | 1 | 1.9 | 4.9 |
| System Pressure (kPa) | | 2450 | 2450 | 2450 | 2450 | 2480 | 2480 | 2480 | 2450 | 2450 | | 2170 - 2450 | | 2310 | 2380 | 4580 |
| Reaction Temp., °C | | 366 | 371 | 377 | 377 | 377 | 382 | 388 | 388 | 388 | 388 | 388 | 393 | 366 | 366 | 366 |
| CH4 rate, cc/min. | | 28 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 | 19 |
| LHSV | | .81 | .83 | .82 | .79 | .80 | .80 | .77 | .79 | .80 | .80 | .80 | .76 | .82 | .77 | .67 |
| H2O Rate cc/hr | | – | – | – | – | – | – | – | .3 | .3 | .3 | – | – | – | .3 | 15 |
| *Yield, wt.* | | | | | | | | | | | | | | | | |
| Methane | | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| Ethane | | .07 | .11 | .10 | .10 | .09 | .09 | .10 | .10 | .07 | .11 | .11 | .12 | .09 | .09 | .09 |
| Ethene | | .08 | .13 | .11 | .08 | .06 | .03 | .03 | .03 | .02 | .03 | .03 | .03 | .11 | .10 | .09 |
| Propane | | .85 | 1.50 | 1.33 | 1.08 | .80 | .35 | .37 | .31 | .17 | .28 | .33 | .30 | 1.60 | 1.24 | 1.20 |
| Propene | | .53 | 1.04 | 1.06 | .99 | .89 | .41 | .26 | .38 | .16 | .17 | .15 | .12 | .72 | .85 | 1.06 |
| Isobutane | | 1.13 | 1.61 | 1.31 | .94 | .60 | .24 | .30 | .23 | .11 | .20 | .21 | .16 | 1.98 | 1.52 | 1.24 |
| n-Butane | | 1.20 | 1.98 | 1.78 | 1.38 | .98 | .40 | .42 | .31 | .16 | .24 | .25 | .20 | 2.11 | 1.65 | 1.63 |
| I-Butene | | .18 | .34 | .37 | .34 | .32 | .14 | .09 | .11 | .05 | .05 | .05 | .03 | .24 | .28 | .38 |
| Isobutene | | .72 | 1.41 | 1.42 | 1.21 | .98 | .43 | .31 | .34 | .17 | .18 | .16 | .12 | .96 | 1.11 | 1.37 |
| Trans-2-Butene | | .37 | .71 | .83 | .73 | .65 | .29 | .20 | .23 | .11 | .10 | .09 | .06 | .51 | .61 | .85 |
| Cis-2-Butene | | .25 | .48 | .56 | .49 | .44 | .20 | .14 | .16 | .07 | .07 | .06 | .04 | .34 | .41 | .52 |
| | *Feed* | | | | | | | | | | | | | | | |
| Total Gas (C4) | | 5.4 | 9.3 | 8.9 | 7.4 | 5.8 | 2.6 | 2.2 | 2.2 | 1.1 | 1.4 | 1.4 | 1.2 | 8.7 | 7.8 | 8.4 |
| C5 - 166°C | | | | | | | | | | | | | | | | |
| 166°C - 427°C | | | | | | | | | | | | | | | | |
| 427°C+ | | | | | | | | | | | | | | | | |
| C5 - 343°C | | | 23.6 | | | | | | | | | | | | | |
| 343°C | 100 | | 67.1 | | | | | | | | | | | | | |
| *Pour Point* °C | | | | | | | | | | | | | | | | |
| As drained | 46 | 10 | 16 | 16 | 18 | 27 | 32 | 35 | 41 | – | – | 41 | 43 | 10 | 4 | 4 |

AIR REGENERATION

## *EXAMPLE IV*

A catalyst was prepared by steaming the ammonium form of ZSM-5 (silica:alumina ratio of 70:1, alpha of 170) with 100 percent steam at 450°C for 16 hours. The steamed zeolite was then added to a 1N ammonium nitrate solution, pH about 4, and maintained in this solution at 93°C for 4 hours. The liquid was then decanted and the catalyst washed with deionized water. The ammonium form ZSM-5 so produced was than calcined in nitrogen at temperatures increasing from 25°C to 538°C at a rate of 1°C min.$^{-1}$ and held at the final temperature for 5 hours. The resulting hydrogen from zeolite (alpha of 65) was then sodium exchanged using 0.25N aqueous sodium bicarbonate solution to an alpha value of about 1.

The above catalyst was used to hydrocrack hexadecane at 370°C, 5340 kPa, LSHV 1.0 hr$^{-1}$, in the presence of hydrogen. The hydrocracking proceeded readily with an equilibrium conversion of about 46%, as shown in Figure 5. The addition of 5,6-benzoquinoline in an amount equivalent to 4 ppm of nitrogen as a poison after about 37 days on stream reduced the hexadecane conversion to 35%, as shown in Figure 5. Successively greater amounts of benzoquinoline, equivalent to 8, 47, 48 and 500 ppm of nitrogen were added to the feed after 39, 45, 53 and 54 days on stream, as indicated in Figure 5. The poison was fed in continuously at the specified rate.

Water was then co-fed with the feedstock at the rate of 5 percent by volume for 25 hours after 60 days on stream. This resulted in an increase in conversion from 35% to 54%, as shown, regardless of the fact that 500 ppm of benzoquinoline was still present in the feed.

After 81 days on stream, the conditions were changed by raising the temperature to 370°C with 500 ppm of nitrogen as cyclohexylamine continuously present in the hexadecane feedstock. Cyclohexylamine is a more basic nitrogen poison than the benzoquinoline and therefore is more deleterious to catalyst activity. The equilibrium conversion under these conditions was about 10 percent, as shown in Figure 6.

Addition of water for 24 hours at 86 days on stream (0.35 cc. hr$^{-1}$ 7 volume percent of feed) produced an increase in catalyst activity, resulting in an equilibrium conversion of about 19 percent, as indicated by the symbol "100/0" in Figure 6. After the conversion had decreased to about 11 percent at 100 days addition of 0.25 cc. hr$^{-1}$ water for about 24 hours brought the conversion back up to about 14 percent.

Mixtures of water and methanol were then added to the feed starting with an 80/20 water/methanol mixture at 0.22 cc. hr$^{-1}$, 5 volume percent of feed after about 97 days on stream. The activity increased after addition of the mixture terminated, to about 30 percent before decreasing gradually to about 19 percent at about 105 days on stream.

A 60/40 water/methanol mixture was added to the feedstock for about 24 hours at the rate of 0.25 ml. hr$^{-1}$, 5 volume percent of feed, to restore the activity, resulting in a maximum equilibrium conversion of about 24.4 percent at 108 days on stream.

An 80/20 water/methanol mixture was added to the feedstock for about 24 hours at the rate of 0.25 ml. hr$^{-1}$, 5 volume percent of feed, to restore the activity, resulting in a maximum equilibrium conversion of about 31 percent at 120 days on stream.

When the conversion had decreased to about 9.0 percent at 138 days on stream, the addition of a 90/10 water/methanol mixture to the feedstock for about 24 hours at the rate of 0.25 ml. hr$^{-1}$, 5 volume percent of feed, restored the activity with a maximum equilibrium conversion of about 26 percent at about 140 days on stream.

These results show that the mixture of water and methanol as a water precursor is more effective than water alone in restoring and maintaining catalytic

activity. Although the effect of the activation is shown here in the change in equilibrium conversion, the process could be operated at constant conversion with the operating parameters being altered to achieve this. If this were done, the operating temperature could be lowered as the catalyst became activated.

*EXAMPLE V*

The hexadecane cracking described in Example IV was continued at a temperature of 370°C, 5340 kPa, LHSV 1.0 $hr^{-1}$ in the presence of hydrogen, using n-hexadecane containing 500 ppm nitrogen in the form of cyclohexylamine as the feed.

When the conversion of hexadecane had fallen to about 9 percent at 159 days on stream, methanol was added to the feed at the rate of 0.25 ml. $hr^{-1}$, 5 volume percent of feed, for one day. The addition of the methanol resulted in a maximum equilibrium conversion of about 20 percent at 164 days on stream. The conversion thereafter declined to 9.7 percent at 172 days on stream. Figure 7 shows the conversion obtained from about 110 to 180 days on stream. Comparison of Figures 5, 6 and 7 shows that the use of a mixture of water and methanol as a water precursor is more effective at restoring activity than the use of water or methanol alone.

CLAIMS

1. A method for activating a crystalline zeolite catalyst employed in a hydrocarbon conversion process in which a hydrocarbon is contacted with the zeolite under conversion conditions of elevated temperature and pressure, which method comprises contacting the zeolite with (i) water or hydrogen sulfide and/or (ii) a precursor of water or hydrogen sulfide.

2. A method according to claim 1, in which the zeolite is contacted with water and/or a water precursor.

3. A method according to claim 2, in which the water and/or water precursor is co-fed to the zeolite with the hydrocarbon.

4. A method according to claim 3, in which the water and/or water precursor is co-fed with the hydrocarbon at periodic intervals.

5. A method according to any one of claims 1 to 4, in which the water precursor is an alcohol.

6. A method according to claim 5, in which the water precursor is methanol, ethanol, propanol, butanol or pentanol.

7. A method according to any one of claims 1 to 6, in which the zeolite is contacted with a mixture of water and a water precursor.

8. A method according to claim 7, in which the weight ratio of the water to the water precursor is from 10:90 to 90:10.

9. A method according to any one of claims 1 to 8, in which the zeolite has a silica:alumina ratio of at least 12 and a Constraint Index of 1 to 12.

10. A method according to any one of claims 1 to 9, in which the zeolite is ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, or ZSM-38.

11. A method according to any one of claims 1 to 8, in which the zeolite is zeolite beta.

12. A method according to any one of claims 1 to 11, in which the zeolite has been steamed to reduce its alpha value to not less than 10 and then cation-exchanged with an alkali metal cation to reduce its alpha value to less than 10.

13. A method according to claim 12, in which the steamed zeolite is cation exchanged with an alkali metal cation to reduce its alpha value to less than 5.

14. A method according to claim 12, in which the steamed zeolite is cation exchanged with an alkali metal cation to reduce its alpha value to less than 1.

15. A method according to any one of claims 1 to 14, in which the hydrocarbon conversion process comprises hydrocracking.

16. A method according to any one of claims 1 to 14, in which the hydrocarbon conversion process comprises catalytic dewaxing.

17. A hydrocracking process which comprises contacting a hydrocarbon feedstock under hydrocracking conditions of elevated temperature and pressure and in the presence of hydrogen with a hydrocracking catalyst comprising a crystalline zeolite component and a hydrogenation component, characterized in that the catalyst is activated by periodically co-feeding with the hydrocarbon feedstock a mixture of water and a water precursor which forms water at the conditions employed, the weight ratio of the water to the water precursor in the mixture being from 10:90 to 90:10.

18. A process for dewaxing for high pour point hydrocarbon feedstocks which comprises contacting the hydrocarbon feedstock under dewaxing conditions of elevated temperature and pressure with a dewaxing catalyst comprising a crystalline zeolite, characterized in that the catalyst is activated by periodically co-feeding with the hydrocarbon feedstock a mixture of water and a water precursor which forms water at the conditions employed, the weight ratio of the water to the water precursor in the mixture being fromm 10:90 to 90:10.

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| Division : | |
| Main : | 018, |
| Seg1 : | 121 |
| Seg2 : | |
| Project : | |
| Job Number : | |
| App Code : | |
| Source : | |
| Doc Id : | |
| Cycle Date : | |
| Cycle : | |
| Descr1 : | |
| Descr2 : | |
| Descr3 : | |
| Amount : | |
| Month : | July 2004 Y-T-D |

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